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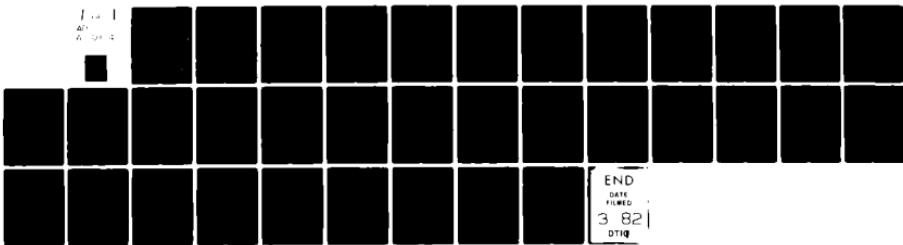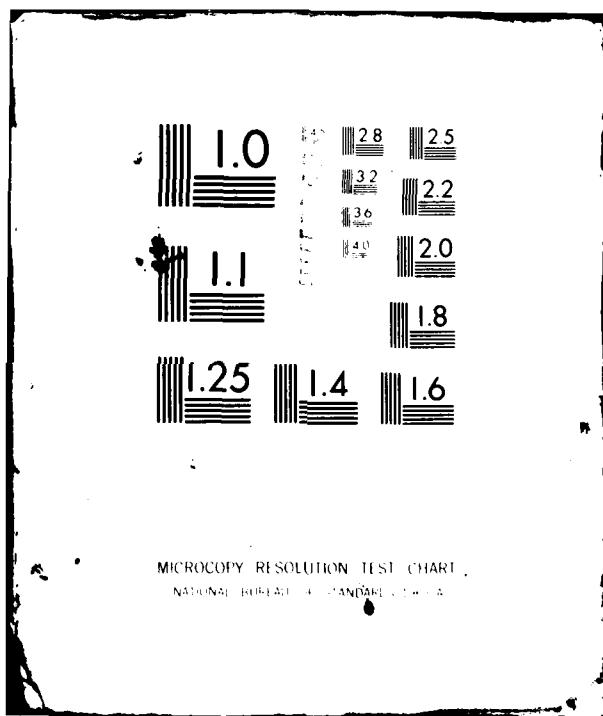
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COMPENSATION FOR DRIFT AND

INTERFERENCES IN MULTICOMPONENT ANALYSIS

by

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The detection and subsequent correction of drift in an analytical signal occurring during the course of an analysis is a common problem in analytical chemistry. In this paper, a solution to this problem is presented in the form of an extension to the theory of the Generalized Standard Addition Method (GSAM), a method currently used to simultaneously correct for matrix effects and interferences in multicomponent analysis. Additionally, the GSAM has been extended to detect and correct for normally unwanted

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interference effects by using more sensors (wavelengths, electrodes, etc.) than there are analytes. Standard additions of a pseudo-analyte containing all potential interfering components in a sample can be used to correct for all potential interferences at once.

Brief

An extension of the Generalized Standard Addition Method is made to include usage of more sensors then analytes and signal drift detection and correction.
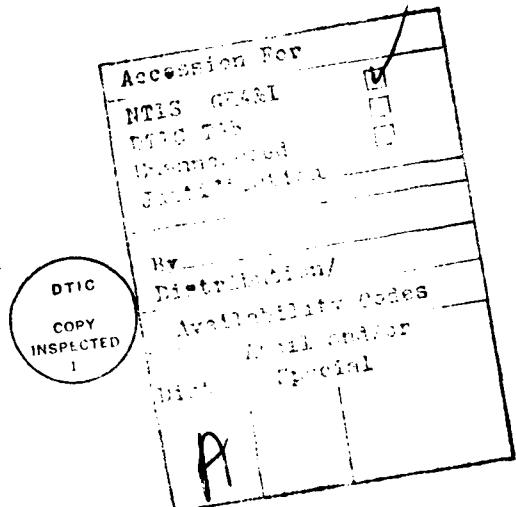
Abstract

The detection and subsequent correction of drift in an analytical signal occurring during the course of an analysis is a common problem in analytical chemistry. In this paper, a solution to this problem is presented in the form of an extension to the theory of the Generalized Standard Addition Method (GSAM), a method currently used to simultaneously correct for matrix effects and interferences in multicomponent analysis. Additionally, the GSAM has been extended to detect and correct for normally unwanted interference effects by using more sensors (wavelengths, electrodes, etc.) than there are analytes. Standard additions of a pseudo-analyte containing all potential interfering components in a sample can be used to correct for all potential interferences at once.

INTRODUCTION

Until fairly recently, analytical chemists have used laboratory computers primarily for data acquisition, storage and retrieval. Presently, a growing awareness and application of such topics as experimental design, optimal control and multivariate data analysis promises to expand the role of computers in chemical analysis. With greater utilization of the computational and logic-based decision-making abilities of computers, a new generation of what might be called intelligent analytical instrumentation will evolve with the ability to detect and correct for problems that may render an analysis invalid.

One well-known problem is drift in an analytical signal occurring over a period of time in which a sample is analyzed. This is called short term drift as opposed to long term drift which occurs from sample to sample or day to day. When the simple Standard Addition Method or the Generalized Standard Addition Method (1) is used, long term drift is not a problem as calibration and analysis is performed simultaneously for each sample. Short term drift may be a consequence of various factors -- temperature, electronic drift in detectors, changes in optical alignment and other causes depending on the analytical instrument of interest. Without proper drift correction in quantitative chemical analysis, a time-dependent systematic (non-random) error is introduced. To compensate for drift, prior knowledge of its presence must be available. This is a severe limitation. Most certainly, a method is needed that can detect the presence of short term drift, characterize the drift, and simultaneously correct for it. Ideally, this method should be applicable to multicomponent chemical analysis.

Recently, our laboratory has developed an experimental design and data analysis procedure that is capable of fulfilling these requirements (1,2).

It is a generalization based on the method of standard additions and can include any number of analytes. It is referred to as the Generalized Standard Addition Method (GSAM) and was originally developed to correct for matrix effects and interferences (i.e., chemical, physical, and spectral interferences) arising from chemical species in the sample. It has been applied to spectrophotometry (2), inductively coupled plasma-atomic emission spectrometry (ICP-AES) (3), ion-selective electrode potentiometry (4), and anodic stripping voltammetry (5). In this work, the GSAM is extended to detect and correct for interferences that do not originate from chemical species present in the sample (i.e., instrumental drift).

When the response from an analytical sensor is drifting for one reason or another, the response is a function of the concentrations of analytes and interfering components, and the cause of the drift (time, temperature, etc.). Before a drift correction can be made, the drift must be detected in much the same way as the analyte or an interferent is detected. The problem is one of detecting the drift, a nonrandom signal, in the presence of the random noise inherent to the sensor. To test the potential of the GSAM to solve the drift problem, it was necessary to use computer simulated experiments generating carefully controlled data to be analyzed. This is exactly analogous to preparing primary standard samples in order to test the recovery or detection limits of a new analytical method. The method used to simulate the multicomponent analysis and the results obtained from the GSAM are given in a later section along with results using experimentally obtained data.

In addition to the use of the GSAM for detection and correction of

short term drift, this paper will also extend the theory of the GSAM for the case where the number of sensors (p) is greater than the number of analytes (r).

A common problem in chemical analysis is the presence of potential interfering species not expected in the sample. This is an ideal case for using more sensors than analytes. For example, in the routine analysis of two analytes using the GSAM, standard additions of two standards corresponding to the two analytes should be made. But if potential interfering chemical species are present, experimentally recovered concentrations could be in error. By using more sensors than analytes, this paper will show how the GSAM can be used to indicate the presence of potential interferants and correct the analyte concentrations accordingly.

Background and Theory

The Generalized Standard Addition Method

The theory of the GSAM has been presented in full detail in previous papers (1,2). Therefore, only a basic review is given here. The GSAM requires that for r analytes, the responses from p sensors (p $\geq$ r) be recorded before and after n standard additions are made (n $\geq$ r). The model is

$$r_{m,\ell} = \sum_{s=1}^{r} c_{m,s} k_{s,\ell} \qquad \begin{array}{l} m=1,\ldots,n \\ \ell=1,\ldots,p \end{array} \qquad (1)$$

where $r_{m,\ell}$ is the response of the ℓth sensor after the mth addition of analyte (or interfering component) s. $c_{m,s}$ is the concentration of the sth component and $k_{s,\ell}$ is the linear response constant for the ℓth sensor to the sth component. Representing the above in matrix notation gives

$$R = CK \qquad (2)$$

where R is the (n + 1) x p matrix of measured responses (initial responses plus the responses following the n additions), C is the (n + 1) x r concentration matrix, and K represents the r x p matrix of linear response constants showing the contribution of each of the r analytes to each of the p sensors for a given sample matrix.

Since concentrations are not always additive, volume corrected responses are used. Equation (1) can be rewritten as

$$r_{m,\ell} = \sum_{s=1}^{r} \frac{n_{m,s}}{V_m} k_{s,\ell} \qquad (3)$$

where $n_{m,s}$ is the total number of moles of component s, and V_m is the volume after the mth addition. This can be expressed as

$$q_{m,\ell} \equiv V_m r_{m,\ell} = \sum_{s=1}^{r} n_{m,s} k_{s,\ell} \qquad (4)$$

which can be separated into

$$q_{m,\ell} = \sum_{s=1}^{r} \Delta n_{m,s} k_{s,\ell} + \sum_{s=1}^{r} n_{o,s} k_{s,\ell} \qquad (5)$$

where $\Delta n_{m,s}$ is the total amount of component s added and $n_{o,s}$ is the initial number of moles of component s. Now

$$q_{o,\ell} \equiv V_o r_{o,\ell} = \sum_{s=1}^{r} n_{o,s} k_{s,\ell} \qquad (6)$$

with V_o representing the initial volume of the sample before any additions are made and $r_{o,\ell}$ the initial response of the ℓth sensor. Equation (5) can now be written as

$$q_{m,\ell} = \sum_{s=1}^{r} \Delta n_{m,s} k_{s,\ell} + q_{o,\ell} \qquad (7)$$

Considering only the <u>changes</u> in responses gives,

$$\Delta q_{m,\ell} = \sum_{s=1}^{r} \Delta n_{m,s} k_{s,\ell} \qquad (8)$$

In matrix notation,

$$\Delta Q = \Delta N K \qquad (9)$$

where ΔQ is nxp, ΔN is n x r, and k is r x p. Using the method of multiple linear least squares to solve for K in the presence of an overdetermined system (n>r), the generalized inverse of ΔN (6) is needed resulting in,

$$K = (\Delta N^T \Delta N)^{-1} \Delta N^T \Delta Q \qquad (10)$$

where the generalized inverse of the matrix ΔN is defined as $(\Delta N^T \Delta N)^{-1} \Delta N^T$.

After K is found, the vector of initial analyte quantities, $\underrightarrow{n_o}$, is recovered by solving (when r = p)

$$\underrightarrow{n_o} = \underrightarrow{q_o} K^{-1} \qquad (11)$$

Therefore, to perform an analysis using the GSAM, three conditions must be met:

(1) $n \geq r$, (2) the standard additions must span the r dimensional concentration space ($\Delta N^T \Delta N$ must have rank r), and (3) each analyte must effect a response from at least one sensor ($\Delta Q^T \Delta Q$ must have rank r).

The GSAM is a very simple method to employ. To determine one row of an r x p K matrix (the sensitivities of the p sensors to the sth component), only one addition containing the analyte is required while recording all the sensor's responses. Equation 10 then simplifies to

$$\underrightarrow{k} = \frac{1}{\Delta n} \cdot \underrightarrow{\Delta q} \qquad (12)$$

This process can be repeated n = r times making standard additions of each analyte only once permitting the determination of K and thereby allowing $\underrightarrow{n_o}$ to be estimated. Unfortunately, utilizing this simple approach the analyst has obtained just sufficient data to satisfy the above conditions. With n > r a better estimation of the elements of K is obtained due to the use of an overdetermined system of equations. Nevertheless, the simplified mode of the GSAM permits a very quick estimate of interferences present and initial amounts.

Drift Correction

Only small alterations in the theory of the GSAM are needed to yield a model capable of compensating for drift. For first order drift

equation (3) becomes

$$r_{m,\ell} = \sum_{s=1}^{r} \frac{n_{m,s}}{V_m} k_{s,\ell} + t_m k_{t,\ell} \tag{13}$$

where t_m is the time that has elapsed from the initial measurement up to the mth addition and $k_{t,\ell}$ is the linear response constant of time on the ℓth sensor. Equation (4) becomes

$$q_{m,\ell} = \sum_{s=1}^{r} n_{m,s} k_{s,\ell} + V_m t_m k_{t,\ell} \tag{14}$$

and equation (6) is modified to give

$$q_{o,\ell} = \sum_{s=1}^{r} n_{o,s} k_{s,\ell} + V_o t_o k_{t,\ell} \tag{15}$$

where t_o is the initial time. Usually, the last term will be zero as t_o will be started at zero. Equation (14) can be expanded to give

$$q_{m,\ell} = \sum_{s=1}^{r} \Delta n_{m,s} k_{s,\ell} + \sum_{s=1}^{r} n_{o,s} k_{s,\ell} + V_m t_m k_{t,\ell} \tag{16}$$

Subtracting equation (15) from equation (16) results in

$$\Delta q_{m,\ell} = \sum_{s=1}^{r} \Delta n_{m,s} k_{s,\ell} + (V_m t_m - V_o t_o) k_{t,\ell} \tag{17}$$

Using matrix notation equation (9) is again obtained except in this case ΔN is now $n \times (r+1)$ where the entries in the $(r+1)$th column are $(V_m t_m - V_o t_o) \equiv \Delta t_{m,r+1}$ for the mth addition and K becomes $(r+1) \times p$ with the $(r+1)$th row estimating the effect of time on each of the p sensors. In the general case, the above equations can be modified to include combinations of higher order functions of time. For these instances, the model (eq.(1)) becomes

$$r_{m,\ell} = \sum_{s=1}^{r} c_{m,s} k_{s,\ell} + \sum_{i=1}^{w} t^i k_{t^i,\ell} \qquad (18)$$

where w represents the order of the drift process.   t should be noted
that the model can be modified to include other parameters that could
cause drift, i.e. temperature cycling.

Equation (10) is still used to solve for K. However, since there is
no time sensor, the respective rows of K containing response constants
for time must be deleted before using equation (11) to solve for n_o.
These deletions are allowed because by making the "time additions" (including time
in the model), K is corrected for drift and there is no need of the k_{t^w}
rows. Nevertheless, k_{t^w} is quite important. In view of the fact that
k_{t^w} represents drift, inspection of k_{t^w} will reveal to the analyst whether
or not drift is present in any of the p sensors. Student t-tests can be
performed to detect if a specific $k_{t^w,\ell}$ is significantly different from
zero implying the presence of drift. Thus. the GSAM will inform the
operator when drift is present and concurrently correct for it. When used
in an automated system, the computer can intelligently correct for drift
and flag the sensor as   potentially defective.

With the inclusion of the so-called time additions, the three guide-
lines mentioned earlier become (1) n≥ (r+ number of time parameters).
(2) $\Delta N^T \Delta N$ must have rank (r + number of time parameters), and (3) remains
the same ($\Delta Q^T \Delta Q$ must have rank r)

In a recent publication (2), different variations of the GSAM were
introduced. Due to the consumption of sample inherent with some instrumentation,
(i.e. ICP-AES), and for reasons to be considered later in the paper, the
incremental difference computation partition GSAM (IDC-PGSAM) was the
most appropriate variant to use.

The IDC dictates that the entries of ΔN and $\underrightarrow{\Delta t}$ are just the amounts added or time elapsed since the previous addition. Likewise, the ΔQ entries for IDG-PGSAM are the incremental differences in the volume corrected response from the previous responses. The PGSAM consists of partitioning the sample into r aliquots with additions of only one standard for each aliquot.

More Sensors than Analytes (p > r)

To use more sensors than analytes, the GSAM requires trivial alterations in the equations. Equations (1) through (10) remain the same. Solving for $\underrightarrow{n_o}$, however, requires a new procedure. Since p > r, K is not a square matrix and consequently K^{-1} no longer exists invalidating equation (11). Therefore a generalized inverse of K is needed which will allow the estimatation of $\underrightarrow{n_o}$ as

$$\underrightarrow{n_o} = \underrightarrow{q_o} K^T [KK^T]^{-1} \qquad (19)$$

where the generalized inverse of the K matrix is defined as $K^T(KK^T)^{-1}$. The guidelines on the number, composition, and order of the n multiple standard additions become (1) remains the same ($n \geq r$), (2) ($\Delta N^T \Delta N$ must have rank r), and (3) $\Delta Q^T \Delta Q$ must have rank $\geq$ r. The IDC-GSAM was the variation used in the p > r study (all standard additions are made to the same sample).

Detection of Potential Interferences

The GSAM will correct for the interferences during a multicomponent analysis only if the interferences are anticipated prior to analysis. Correction for totally unaccounted for interferences is considerably more complicated depending upon how the interfering species affects the sensors.

If the goal of a routine analytical procedure is the analysis of

r analytes and U additional potential interferents can be identified, then the GSAM can be modified to detect and correct for the presence of one or more of the U potential interferents during the analysis of the r analytes.

Major modifications are not necessary in order to incorporate this new improvement into the GSAM. Equations (1) through (11) essentially remain the same. The main alterations required lie in the experimental design. For instance, if two analytes are involved ($r = 2$), then two sensors ($p = 2$) and two or more standard additions ($n \geq 2$) would normally be chosen. For detection and correction of unaccounted potential interferents present in the sample, additional sensors yielding responses to the potential interferents are obviously required along with at least one extra standard addition consisting of a pseudo-analyte. This pseudo-analyte should consist of one solution containing all of the U potential interferents. The responses for all sensors are recorded as usual. Averaging the extra responses for the potential interferents to form one pseudo-reponse and therefore one pseudo-sensor, and making only one standard addition containing all the U anticipated interferences, the dimension of ΔQ, ΔN, K become respectively, n x (p+1), n x (r+1) and (r+1) x (p+1). Provided additions of all potential analytes are made, the estimated n_o will be interference corrected with the moles of pseudo-analyte corresponding to the average moles of all potential interferents. Naturally, when none of the U interferents are present, the GSAM estimated moles for the pseudo-analyte will be zero. If one or more potential interferents are present, the pseudo-analyte will be non-zero and the primary analytes will be correctly determined. This procedure makes no provision for determining exactly which of the pseudo-analyte interferent is actually present in the sample. Only the primary analytes are of interest.

EXPERIMENTAL

All calculations were done using "GSAM", a Fortran IV program available from Infometrix, Inc., P.O. Box 25808, Seattle, WA 98125. All computations were performed on the Department of Chemistry, VAX 11/780 computer.

Time Drift Study

All "synthetic" data from computer simulated analyses (ΔQ as expressed in eq. (9)) were based on known K and ΔN matrices. Three analytes were examined with three standard additions of 1 unit each per analyte. A second order time model was used in this study. Linear time additions consisted of 1 unit of time (units are arbitrary) between additions of analyte in a given partition with 2 units of time elapsing between partitons. Quadratic time additions were performed in a similar manner. Volumes were kept constant. A 2% quadratic drift was incorporated into the synthetic data responses (no random noise) of sensor three corresponding to analyte three and a 2% linear drift was simulated in sensor one corresponding to analyte 1. Random noise was introduced to the simulated data responses by using a Monte Carlo method (7). A normal distribution was assumed with a mean zero and a standard deviation equal to a 1% relative standard deviation (RSD) of the noise-free synthetic data responses. A 1% RSD is the estimated precision of many analytical instruments. Twenty Monte Carlo perturbations were performed to compute twenty random responses. From the final results using the twenty Monte Carlo responses, standard deviations were estimated for n_o and K.

Table I lists the synthetic data before introduction of random noise. As mentioned earlier, the IDC-PGSAM experimental design was used.

Al-As-Cd Matrix and Time Study

The ICP-AES and experimental operating conditions used have been described elsewhere (3). Also presented in this reference is the procedure of additions and solution concentrations. A brief summary of the experimental design is listed in Table II. Time additions consisted of three minutes between analyte additions and five minutes between partitions. A 10% linear drift was mathematically added to the Al sensor. Standard deviations for $\underrightarrow{n_o}$ and K were calculated with the Monte Carlo method using twenty perturbations with a RSD equal to 1%, the estimated precision of our ICP instrument.

Potential Interferences Study

The time independent data (no drift) used in the simulated time study (Table I) was used. Sensor three represented the pseudo-sensor. Only one standard addition composed of all unforeseen analytes was made. Random responses were calculated as stated above.

RESULTS AND DISCUSSION

Time Drift Study

Four simulated experiments were performed in order to test the ability of the GSAM to detect and correct for time drift while avoiding over compensation when drift is not present. They consisted of: no time additions and no drift; time additions but no drift; no time additions and with drift present; and time additions with drift. Results from these four studies are presented in Tables III, IV, V and VI, respectively. Before examining the results given in the Tables, some clarification of the experimental procedure is necessary. From the experimental section it is noted that the IDC-PGSAM was used and the corresponding $\underrightarrow{\Delta t}$ in ΔN are incremental. Namely, the time elapsed since the previous measurement is used for the entries in the $\underrightarrow{\Delta t}^W$. For the second partition the first linear time addition (fourth time addition overall) coinciding to the first standard addition of the same partition is five units of time and not the expected two units. This is true since the partitions are thought of as new samples and Δt^W in this case is the time elapsed since the initial reading was recorded (three units plus two units for the time expired between partitions). The change in the increments of time between partitions is necessary to preserve the non-singularity of $(\Delta N^T \Delta N)^{-1}$. Analogous inference is given to the other entries of the $\underrightarrow{\Delta t}$ corresponding to the additional partitions and to $\underrightarrow{\Delta t}^2$. Also, while monitoring the time between additions it is assumed that during the brief instant required for measurement of the signal, drift is negligible.

From Table I it is observed that no units of time have been ascribed to $\underrightarrow{\Delta t}^W$. Actually, the units for $\underrightarrow{\Delta t}^W$ are immaterial. Units of time only alter the magnitude of $k_{\underrightarrow{t}}$ and $k_{\underrightarrow{t}2}$ (last two rows of K, effect of time or drift on each sensor) and

not the k_r's which remain constant. The magnitude of the entries in
$\underset{\rightarrow}{\Delta t}$ or $\underset{\rightarrow}{\Delta t^2}$ (decided by the units used) will then dictate the magnitude
of drift seen, if any, in the sensors. Therefore, the changing $\underset{\rightarrow}{k_t}$ or
$\underset{\rightarrow}{k_{t^2}}$ with units of time are of no consequence since $\underset{\rightarrow}{k_t}$ and $\underset{\rightarrow}{k_{t^2}}$ are
deleted from K before calculating $\underset{\rightarrow}{n_o}$ and the $\underset{\rightarrow}{k_r}$'s remain time-corrected.

Finally, from Table I it is seen that an additional sensor to
account for time additions is not needed. To use a time sensor would only
allow the calculation of t_o, but t_o is already known.

The results in Table III show the performance of a normal run of the
GSAM, that is, before time additions are made and drift is simulated. The
small relative errors in $\underset{\rightarrow}{n_o}$ and the standard deviations of $\underset{\rightarrow}{n_o}$ indicate
that the GSAM can easily tolerate 1% random noise without introducing
large errors or uncertainties in $\underset{\rightarrow}{n_o}$. A t-test at the 95% confidence
level, shows that $k_{2,1}$, $k_{3,1}$, and $k_{1,3}$ ($k_{row, column}$) are not significantly
different from zero as expected according to Table I.

Table IV exhibits the results when there is uncertainty about the
presence of drift. That is, time additions are made without prior
knowledge of the existence of drift. Once again, using t-test (at the 95%
confidence level) will show that $k_{2,1}$, $k_{3,1}$, $k_{1,3}$, $\underset{\rightarrow}{k_t}$, and $\underset{\rightarrow}{k_{t^2}}$ are not
statistically different from zero. Also, a standard t-test at the 95%
confidence level indicated that there is no statistical difference in $\underset{\rightarrow}{n_o}$
from Tables III and IV.

Table V clearly shows that the errors incurred if drift is present
and no time additions are made to compensate for the drift are large
indeed. $k_{2,1}$, $k_{3,1}$, and $k_{1,3}$ are now significantly different from zero.
Although the rest of K is approximately equal to the previous K, K^{-1} is
seen to be substantially dissimilar to K^{-1} represented in Tables III and IV
Accordingly, since K^{-1} is used in estimating $\underset{\rightarrow}{n_o}$, the errors in $\underset{\rightarrow}{n_o}$ are

greatly enhanced.

Finally, Table VI presents the results when time additions are made and drift is present. $k_{2,1}$, $k_{3,1}$, and $k_{1,3}$ are once again not statistically different from zero and the GSAM has correctly characterized the magnitude of the existing drift. Specifically, $k_{t,1}$ and $k_{t^2,3}$ are approximately equal to 0.02. K^{-1} is back to its correct form (time-corrected) and $\underrightarrow{n_o}$ is accurately determined.

From the results presented it appears the GSAM can detect, characterize, and correct for drift in the presence of sample related interferences and random noise. Other studies were performed to determine the quantity of random noise permissible before the GSAM would fail. With the K in Table I, up to 5% random noise could be tolerated before relative errors in $\underrightarrow{n_o}$ approached 8%.

However, another variant of the GSAM commonly used in analysis is the IDC-GSAM where the sample is no longer partitioned, and all standard additions are made to the same sample solution. IDC-GSAM was found to be inappropriate <u>when making</u> time additions. With only 1% random noise, errors as high as 30% in $\underrightarrow{n_o}$ were obtained. The inadequacy of the IDC-GSAM to differentiate the systematic drift from the 1% random noise is an artifact of the experimental design, particularly, the perturbations performed on R. Because the IDC-GSAM volume-corrected responses can be successively increasing thoughout the standard additions, the noise introduced is subsequently also accumulative, thereby suggesting that the IDC-GSAM is very sensitive to measurement noise. For IDC-PGSAM, the sample is partitioned yielding additive volume-corrected responses accumulating for

only one partition and reponses are reduced back to the initial values
before a series of standard additions are made to a new partition. Thus
the noise introduced is no longer accumulative for the period of the analysis
but only increasing during additions to a partition. Accordingly, when
time additions are made, the IDC-PGSAM is the method of choice.

Three studies were done to test the applicability of the GSAM drift
correction to ICP-AES. These were: no drift present with time additions;
10% drift in the Al sensor without time additions; and 10% drift in the
Al sensor with time additions. Table VII contains the final results for
the above studies. Spectral interferences occurring were the well-documented
interferences of direct spectral overlap of As (228.812 nm) on Cd (228.802 nm)
and the continuum emission of Al effecting As (193.696 nm) (8). A previous
study demonstrated the applicability to GSAM to characterize and correct
for these interferences (3).

The results of this study indicate that when time additions are made,
with drift present or not present, accurate n_o's are estimated. With the
occurrence of drift, and time additions are not included, the n_o's are
largely distorted. Thus, the GSAM can be used to accurately correct for
instrumental drift in ICP-AES in the presence of sample dependent inter-
ferences.

Potential Interferences Study

As stated in the Experimental Section, the same simulated experiment
used in the time study with no drift and no time additions (Table I) was
used with one minor change here. That is, to exemplify the simplicity of
this extra determination of potential interferences, only one addition
of the pseudo-analyte was made. More standard addition of the pseudo-
analyte may be performed but only one is necessary to determine the
presences of potential interfering analytes. Even though in the Time

Study sensor 3 represented one analyte, this sensor can also be the pseudo-sensor obtained by averaging the responses of several sensors. The number of sensors or responses constituting the pseudo-sensor or pseudo-response is immaterial, for this study, as long as the average pseudo-response equals the response for sensor 3 used in the Time Study. The IDC-GSAM could have been used here, since *no time additions* are made; no statistical differences in the results are expected. Assuming that sensor 3 in Table VIII is the average of many sensors, then the GSAM appears to correct for this potential interference. k_3 (last row of k) would tell the analyst that sensor two could have a significant interference pertaining to some chemical species in the sample if these chemical species are present. $k_{3,3}$ reveals the total sensitivity of all sensors making up the pseudo-sensor. The n_o associated with the pseudo-analyte discloses to the analyst that other species are present in the sample since the pseudo-n_o is significantly different than zero. Thus, further qualitative studies of the sample are necessary to enable the usage of the appropriate *standard addition* for proper quantitative results of the secondary analytes composing the pseudo-analyte. The case with no extra standard addition of the pseudo-analyte was also investigated with the results presented in Table IX. These results show the error acquired in the determination of n_o for analyte two. Clearly, when possible, it seems best to make one extra addition of all conceivable interfering species and average the respective reponses forming the pseudo-response to permit proper correction and detection of the potential analytes.

CONCLUSION

In this paper an extension of the GSAM was presented to correct for drift. This method may be extended to higher order functions of drift provided additions of equal orders are made. The experimental results show that the IDC-PGSAM may be applied when drift is uncertain. With the GSAM, the analyst can detect and correct for potential interferents provided at least one standard addition containing all of these interferents is made. The single extra addition of the pseudo-analyte represents a useful check on the analysis. If the extra sensors required for the check on the analysis are available, they should be used to gain maximum information about the sample.

The incorporation of automatic drift detection and correction, more sensors than analytes, and the compensation of potential interferents in the matrix into the GSAM represents a step toward the development of intelligent analytical instrumentation. The combination of computer con-trolled analytical instrumentation and the advanced GSAM as the chosen analytical experimental design permits instruments to perform self-correcting multicomponent analysis. Studies of this nature are currently underway in our laboratory.

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Table I. Experimental Design for Simulated Time Study (IDC-PGSAM)

	$\overset{\Delta t}{\longrightarrow}$	$\overset{\Delta t^2}{\longrightarrow}$
partition 1	1.0	1.0
	1.0	3.0
	1.0	5.0
partition 2	5.0	25.0
	1.0	11.0
	1.0	13.0
partition 3	9.0	81.0
	1.0	19.0
	1.0	21.0

	K(without drift)			K(with drift)			K^{-1}		
	1	2	3	1	2	3	1	2	3
1	1.0	0.5	0.0	1.0	0.5	0.0	1.0	−0.5114	0.2857
2	0.0	1.0	0.5	0.0	1.0	0.5	0.0	1.143	−0.5714
3	0.0	0.25	1.0	0.0	0.25	1.0	0.0	−0.2857	1.143
t	0.0	0.0	0.0	0.02	0.0	0.0			
t^2	0.0	0.0	0.0	0.0	0.0	0.02			

$\overset{n_o}{\longrightarrow}$		
1.0	0.5	1.0

Table II. Experimental Design for Al-As-Cd Time Study
        (IDC-PGSAM)

	$\Delta N(\mu g)$			Δt(ml minute)	$n_o(\mu g)$	
	Al	As	Cd			
additions	801.3	0.0	0.0	36	Al	2503.
of	801.3	0.0	0.0	48	As	999.7
Al	801.3	0.0	0.0	60	Cd	20.14
additions	0.0	599.4	0.0	168		
of	0.0	599.4	0.0	70		
As	0.0	599.4	0.0	82		
additions	0.0	0.0	101.8	300		
of	0.0	0.0	101.8	92		
Cd	0.0	0.0	101.8	104		

Table III. Final Results with no Time Additions, no Drift,
and 1% Random Noise

$$K(s)$$

	1	2	3
1	1.001 (0.016)	0.5029(0.015)	-0.002333(0.0087)
2	-0.002406(0.0055)	1.007 (0.022)	0.5043 (0.019)
3	-0.004081(0.018)	0.2541(0.048)	1.016 (0.040)

$$K^{-1}(s)$$

	1	2	3
1	0.9986 (0.014)	-0.5715(0.018)	0.2862(0.015)
2	0.0006847(0.011)	1.138 (0.053)	-0.5655(0.044)
3	0.003782 (0.012)	-0.2894(0.066)	1.130 (0.062)

	calcd. $n_o(s)$	relative error %[a]
1	1.003 (0.024)	0.300
2	0.4909(0.053)	1.82
3	0.9903(0.058)	0.970

a) relative error $= 100 \times \dfrac{|true - calcd.|}{true}$

Table IV. Final Results with Time Additions, No Drift,
and 1% Random Noise

$$\underline{K(s)}$$

	1	2	3
1	1.006 (0.012)	0.4993 (0.016)	0.001755 (0.0085)
2	0.001180 (0.0062)	1.003 (0.017)	0.5043 (0.012)
3	0.001514 (0.019)	0.2499 (0.049)	1.003 (0.046)
t_2	-0.007131 (0.012)	0.01114 (0.021)	0.006275 (0.0081)
t^2	0.0006920(0.0013)	0.001603(0.0027)	0.0005720(0.0016)

$$\underline{K^{-1}(s)}$$

	1	2	3
1	0.9946 (0.011)	-0.5662(0.015)	0.2832(0.012)
2	-0.0005412(0.010)	1.142 (0.040)	-0.5753(0.030)
3	-0.001299 (0.021)	-0.2858(0.060)	1.144 (0.066)

	calcd. $n_o(s)$	relative error %
1	0.9889(0.023)	1.11
2	0.5041(0.042)	0.820
3	0.9955(0.068)	0.450

Table V Final Results with No Time Additions, 2%
Quadratic Drift in Sensor 3, 2% Linear
Drift in Sensor 1, and 1% Random Noise

$$K(s)$$

	1	2	3
1	1.023 (0.017)	0.4967(0.0080)	0.5799(0.0058)
2	0.04745(0.0045)	0.9976(0.014)	0.8229(0.010)
3	0.07381(0.0054)	0.2461(0.0055)	1.798 (0.025)

$$K^{-1}(s)$$

	1	2	3
1	0.9875 (0.015)	-0.5456(0.015)	0.2179(0.011)
2	-0.01520(0.0046)	1.139 (0.019)	-0.5207(0.015)
3	-0.03845(0.0033)	-0.1335(0.0055)	0.6185(0.0099)

	calcd. $n_o(s)$	relative error %
1	0.9198(0.022)	8.02
2	0.7212(0.021)	44.2
3	0.3365(0.018)	66.3

Table VI Final Results with Time Additions, 2% Quadratic Drift in Sensor 3, 2% Linear Drift in Sensor 1, and 1% Random Noise

$$K(s)$$

	1	2	3
1	1.005 (0.014)	0.5001(0.013)	0.0004186(0.0099)
2	0.002146 (0.0060)	0.9990(0.016)	0.5009 (0.013)
3	0.0001118(0.027)	0.2593(0.037)	1.018 (0.061)
t	0.01990 (0.0032)	-0.004744(0.0069)	0.008284 (0.0092)
t^2	0.0003465(0.0011)	0.001060(0.0054)	0.01905 (0.0022)

$$K^{-1}(s)$$

	1	2	3
1	0.9964 (0.012)	-0.5723(0.017)	0.2817(0.016)
2	-0.002449 (0.017)	1.151 (0.041)	-0.5677(0.034)
3	0.0003758(0.030)	-0.2962(0.057)	1.132 (0.084)

	calcd. $n_o(s)$	relative error %
1	0.9945(0.022)	0.550
2	0.4917(0.049)	1.66
3	0.9893(0.082)	1.07

Table VII   Final Results for Al-As-Cd Time Study

	calcd. n_o µg			relative error %		
	Al	As	Cd	Al	As	Cd
no drift with time correction	2429.	1020.	20.18	2.95	2.03	0.199
10% drift without time correction	2125.	1028.	19.63	15.1	2.83	2.53
10% drift with time correction	2429.	1020.	20.18	2.96	2.03	0.199

Table VIII. Final Results of Unknown Interference Study

		K(s)	
1	0.9987 (0.017)	0.5010(0.0070)	−0.0005370(0.0053)
2	0.002160(0.020)	1.007 (0.025)	0.4983 (0.0092)
3	0.005021(0.055)	0.2415(0.074)	1.007 (0.043)

	calcd. n_o(s)	relative error %
1	0.9937(0.063)	0.630
2	0.4990(0.096)	0.200
3	0.9958(0.063)	

Table IX. Final Results of Unknown Interference
Study without Pseudo-sensor

	K(s)	
	1	2
1	0.9981 (0.015)	0.4974(0.011)
2	-0.0002085(0.0052)	1.006 (0.015)

	calcd. $n_o(s)$	relative error %
1	1.002 (0.022)	0.200
2	0.7457(0.023)	4.91

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